SCIENCE FOR GLASS PRODUCTION

UDC 666.263.2:66.017

GLASS CERAMIC MATERIALS IN THE CONTEXT OF CONTEMPORARY MATERIAL SCIENCE

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Translated from Steklo i Keramika, No. 9, pp. 8 – 13, September, 2003.

Growth rates of production of up-to-date technical materials of different classes are specified. The main reasons for accelerated development of new materials, including glass ceramics are considered. Principal attention is focused on capabilities and application specifics of various types of glass ceramics (heat-resistant high-strength, clear nanostructured, electrically active, bioactive, constructional) in advanced fields of contemporary engineering, industries, construction, and medicine. Properties of glass ceramics of the above types are specified.

Contemporary science of materials investigates technical materials classified according to their chemical nature, structure, and properties: metals and alloys; polymer materials (plastics and synthetic resins); ceramics, glasses, and composites based on them; concretes and binding materials; granite, marble, wood, and other natural materials; auxiliary materials (lacquers, paints, glues, etc.). Glass ceramics are synthesized inorganic multiphase materials with a polycrystalline structure obtained by guided (catalyzed) crystallization of glasses of certain compositions; their chemical nature and structural specifics are closest to ceramics, therefore, material science, especially abroad frequently considers them as part of new ceramic materials.

The leading place among the structural engineering materials is traditionally occupied by steel and alloys, whose world production in 2001 amounted to 840 million tons. The next position is taken by polymers, whose annual production reaches 110 million tons. The production volume of new ceramics for engineering purposes is significantly lower than that of metals and plastics; in the end of the past century in the USA it amounted to 1.3 million tons. For reference, the annual world production of traditional ceramics (construction, refractory, household) in sum exceeds 4000 million tons. However, in the past decades there has been a steady tendency of increase in the relative share of new sophisticated types of ceramics compared to the share of traditional ceramics. Thus, the average growth rate of production and sales of new ceramics in 1985 – 2000 was over 16% per annum, whereas the growth rate of steel was slightly over 2%, engineering plastics 7%, and the growth rate of the total sphere of new materials, according to the EU estimates, was around 5%. The world market of new ceramics by 2002 had exceeded 50 billion dollars, and about 70% of this market belongs to the most industrialized countries: the USA and Japan. Analysts predict future development of this trend. The same trend is observed when analyzing the progress of glass ceramics, which form part of promising new ceramics.

A faster growth rate of new materials, in particular, that of glass ceramics, compared to traditional materials, is due to some objective factors. One of the most significant factors is the emergence and evolution of new fields of engineering, which require structural materials providing for reliable performance of mechanisms in extreme and critical conditions. A required level of service parameters is frequently unattainable in principle when using traditional materials. This primarily concerns aerospace and aircraft engineering, machine building, fuel and nuclear power sectors that urgently need materials capable or protracted performance under extremely high temperatures (1300 – 2000°C) and under elevated mechanical loads (up to 1500 MPa).

A tendency for replacing traditional engineering materials, primarily ferrous metals and alloys by new materials is observed in consumer production as well; in chemical, petrochemical, and mining industries, in power, electroengineering, construction, etc. This tendency is especially typical of industrialized countries due to a relatively low efficiency of using steel and alloys in many sectors of industry: metals, despite their high strength parameters, have insufficient cor-

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TABLE 1

Parameter	Value	Possible application areas
Heat-resistant high-strength glass ceramics and their composites		
Bending strength, MPa:		Aerospace engineering (aircraft fairing, antenna housing), machine building (parts and units), heat exchangers, heater panels, structural elements in high-temperature machinery, laboratory and kitchen ware
glass ceramic	150 – 400	
composite	350 – 1000	
Crack resistance, K_{1C}, MPa · $m^{1/2}$:		
glass ceramic	2 – 4.5	
composite	4 – 25	
Operating temperature, °C	800 – 1200	
Clear glass ceramics		
Integral transmission in visible spectrum range, %	Up to 90	Astronomical mirrors, lasers, solar batteries, optical media in instrument production, peepholes in thermal machines, light-beam housing, heater panels in electric heaters
TCLE, 10^{-7} K^{-1}	– 4 – 0 – + 6	
Heat resistance, °C	800 – 900	
Electroengineering glass ceramics		
Resistivity at temperature of 20°C, log [Ω · m]	10 – 16	Radio and high-frequency engineering, radar housing, electric insulators, vacuum-dense shells, microcircuit boards, electronic devices, data carriers
Dielectric constant	5.5 – 23.8	
Dielectric loss tangent under 1 MHz frequency and 25°C	0.0003 – 0.0030	
Wear- and chemically resistant glass ceramics		
Abradability, g/cm^2	0.004 – 0.030	Lining for chemical and mining equipment, pump parts, corrosion-resistant pipelines, bearings, textile machine parts
Acid resistance (H_2SO_4), %	99.0 – 99.8	
Alkali resistance, %	84 – 95	
Biological glass ceramic and biocomposites		
Duration of bone ingrowth, weeks	4 – 8	Bone implants and endoprosthesis in surgery and dentistry, compounds filling bone defects, medication-carrying media
Strength, MPa:		
bending	140 – 220	
compressive	600 – 1100	
Elasticity modulus, GPa	80 – 120	
Glass ceramics for construction		
Density, kg/m^3	2500 – 2800	Decorative finish of walls, socles, and structural elements of buildings, flooring, protective facing of walls in interiors with moist or chemically aggressive media
Bending strength, MPa	50 – 180	
Water absorption, %	0	

rosion resistance and refractoriness and get oxidized at around 1000°C, oxidation sometimes becoming catastrophic.

The constantly growing insufficiency of available raw materials for traditional production is another important factor in the development of new materials, including glass ceramics.

The chemical and phase composition, as well as the structure of glass ceramics vary within wide limits, which makes it possible to deliberately design materials with a set of prescribed properties, often unique that are not found in other groups of materials, such as TCLE ranging from -90×10^{-7} K^{-1} to zero and then to 300×10^{-7} K^{-1}, thermal resistance above 1000°C, low density (from 2200 kg/m^3), controlled dielectric properties in a wide frequency range, including microwave frequencies, preset transmission in the visible and infrared spectrum ranges (see Table 1). Along with good service parameters glass ceramics have good technological properties, which makes it possible to use standard glass and ceramics technologies and to produce large-sizes articles up to 10 m in size, articles of a complex configuration, with high accuracy of sizes, articles with different levels of porosity from zero to 50 – 70%. Owing to their good service parameters combined with technological and economic efficiency, glass ceramics belong to especially promising synthetic materials.

Research and development of glass ceramics started in 1950s. In 1957 a publication by the Corning Glass Works (USA) for the first time reported the production of crystallized materials based on silicate glasses. The next two decades witnessed the industrial production of glass ceramics in several industrialized states. The USSR played a leading role and was the first to implement a continuous production of a material for construction called "shlakositall" (slag-glass ceramic).

Today more than 100 brands of this kind of materials are produced in the world, such as pyroceram, photoceram, cervit, hercuvit (USA), zerodur, keran, schott-glasskeramik (Germany), neoceram, neoparies, miraclon (Japan), criston, nucrist (Czech), and sitall, shlakositall, sigran (Russia). These materials are often united by the term "glass ceramics", which stresses their genetic bond with glass and common properties with ceramics.

Despite a substantial progress in the development of theoretical principles for glass ceramics production and a multitude of compositions synthesized (thousands of formulas patented), intense research in this sphere continues in the following directions:

– development of structural and functional glass-ceramic materials with special properties: high-strength composites based on a glass-ceramic matrix; bioactive glass ceramic for medicine; optical media based on glass ceramics with a nanocrystalline structure, etc.

– development of new technologies significantly expanding the possibilities of synthesis of nontraditional compositions, for instance, sol-gel technology, nitration of oxide melts to obtain oxynitride glass ceramics; thermochemical treatment of surface of glass ceramic materials to impart new properties; crystallization of glasses under various external effects to obtain oriented anisotropic glass-ceramic structures;

– identification of new application areas for glass ceramics and designing new products, involving as well the use of computer technology

It is impossible in the framework of a single paper to describe all possibilities and application specifics of glass ceramics. In order to demonstrate a variety of such possibilities ranging from aerospace industry and electronics to medicine and construction, let us analyze some of them

An instance of using glass-ceramic materials in contemporary missile technology is glass-ceramic head antenna caps of supersonic ground-to-air and air-to-air missiles. The majority of ground-based and sea-based anti-aircraft and airborne missiles in industrialized countries are equipped with such caps. Fairing is a most important element determining the tactical and service characteristics of a missile and has to meet a set of requirements regarding its radiotechnical, mechanic, and thermal parameters. These requirements can be met by radiotransparent heat-resistant spodumene and cordierite glass ceramics with a low TCLE $(4 - 57) \times 10^{-7}\,K^{-1}$, bending strength 120 – 260 MPa with a variation coefficient of 8 – 15%, compressive strength 350 – 530 MPa, the initial plastic deformation temperature 900 – 1175°C, residual bending strength at 1200°C more than 40 MPa, and dielectric permeability 5.5 – 7.5. Besides being resistant to high thermal and power loads, glass-ceramic antenna caps are known for stable service properties, primarily radioengineering properties and high erosion resistance under any weather conditions of missile storage and flight (protracted effect of increased humidity and sea weather, dust and rain effect, rate of heating and cooling over 300 K/sec. The use of the glass (based on melt) and ceramic (based on slip) technologies ensures production of large-sized antenna caps up to 1 m high of a complex profile with highly accurate sizes.

A significant drawback of glass ceramics is brittleness and low crack resistance. The critical stress intensity coefficient K_{1C}, which provides a quantitative characteristic for crack resistance of glass and glass ceramics is $1.2\ MPa \cdot m^{1/2}$, whereas this coefficient for metals is equal to $30 - 35\ MPa \cdot m^{1/2}$. The most effective direction of research intended to increasing this parameter is the development of composites based on a glass-ceramic matrix reinforced with strengthening elements: fibers, filaments, disperse particles. Composites containing unidirectional silicon carbide fiber Nicalon exhibit record bending strength (100 MPa) and crack resistance ($25\ MPa \cdot m^{1/2}$) for glass ceramic materials. Further more, the destruction of these composites is step-like in contrast to avalanche-like destruction of brittle bodies (glasses, glass ceramics), which provides for increased reliability. It is also essential for high-temperature engineering that mechanical properties of composites rather than deteriorate at temperatures of 1000 – 1100°C actually improve. Good mechanical properties and high corrosion and oxidation resistance at elevated temperatures in glass ceramic composites coexist with their light weight, which is especially significant for aircraft and aerospace machines. Thus, a decrease in the weight of an aircraft by 1 kg saves $150 in operating an airplane, $300 in a helicopter, $10,000 in a missile or a satellite, and up to $50,000 in a spacecraft.

Efficient use of glass ceramics as optical media in astrophysics, optics, laser engineering is based on their unique spectral characteristics, such as clarity, thermal expansion approaching zero within a wide range of temperatures, and high atmospheric resistance. Several brands of glass ceramics, such as pyroceram, neoceram, zerodur, jena, and STL based on quartz-like solid solutions have an extremely fine crystalline structure (crystal size below 0.05 μm), which provides for its transparency in the visible spectrum range. Owing to their steady linear sizes in heating and cooling, glass-ceramic telescope mirrors with diameters reaching 10 m reliably function regardless of differences between day and night temperatures in various climatic conditions, in particular, in mountainous regions, where many astronomic observatories are located. A laser gyroscope with transparent glass-ceramic elements recently installed in New Zealand allows for registering the smallest fluctuation in the Earth rotation. Schott Glaswerke Mainz (Germany) produces large-size glass ceramic plates with high transmission in the red visible and near IR spectrum ranges, which are used by many household electronics manufacturers as heating panels in electric hot plates instead of metal burners.

Structural parameters of glass ceramics have recently expanded toward minimization when nanostructures with crystals sized 10 – 100 nm have been developed. These small sizes of crystals ensure increased light transparency in material, and specific characteristics of the crystalline phase impart properties to the material that are unusual for clear glass ceramics. Some examples of nanostructural glass ceramics with a crystal size of 10 – 15 nm are recently developed potassium-titanium-phosphate compositions which crystallize with the formation of potassium titanyl-phosphate. This crystalline phase has high optical nonlinearity, which is inherited by the glass-ceramic material. A combination of clarity with

optical nonlinearity makes this material a promising basis for new nonlinear-optical media.

High-clarity spinel glass ceramics with a nanocrystalline structure has been developed in the magnesium-zinc-aluminosilicate system with additives of zirconium and titanium oxides. The size of spinel crystals in this glass ceramics is 10 – 50 nm, as a consequence, its integral light transmission reaches the level of melted quartz (90%), it has high refractoriness (work temperature above 900°C), thermal resistance (TCLE 30×10^{-7} – $50 \times 10^{-7}\ K^{-1}$), and chemical resistance (weight loss at 95°C in 5% HCl is 0.002 mg/cm^3 and in 5% NaOH is 0.46 mg/cm^3). Glass ceramics based on lanthanum fluoride with a crystal size below 15 nm is promising for the production of highly effective solid, in particular, fiber lasers of sky-blue or gray colors. This clear chemically resistant borophosphor-silicate glass ceramics has unique insulating properties: its resistivity (1016 $\Omega \cdot$ m) is higher than that of corundum.

For many years the most promising application areas of glass ceramics have been using their enhanced mechanical strength (glass ceramics for building), heat resistance and controlled softening temperature (heat-resistant, low-melting glass ceramics), and spectral characteristics (clear glass ceramics). Lately substantial progress has been made in the development of functional glass ceramics with specialized properties, which significantly expands their application range. Some typical examples of this are glass ceramics intended for electronics, informational technologies, and medicine. According to many experts, theses are now the most dynamically evolving sectors which largely determine the general progress of up-to-date science of materials.

Glass ceramics in electronic technology were mainly used as insulators, for instance, in making microcircuit boards. This application is based on such properties of these materials as low resistivity and dielectric losses, steady dielectric permeability, sufficient electric and mechanical strength, resistance to aggressive media and radiation. There is now a new trend using glass ceramics as electrically active polar dielectrics (piezo, pyro-, ferro-electrics and electrets) capable of converting various types of energy and serving as information carriers. Their synthesis is based on a possibility of isolating non-center-symmetric crystalline phases in glasses of respective compositions, which ensures electric activity of material. Researchers have already obtained polar stilwellite textures with an exceptionally high pyroelectric factor of merit for a non-monocrystalline material, i.e., 0.3 nKl/(cm$^2 \cdot$ K). At the same time they have low dielectric losses and high resistivity at temperatures up to 300°C.

The pyroeffect of the known types of perovskite ceramics is higher by an order of magnitude than that of stilwellite textures, however, their dielectric permeability is higher by 1.5 – 2 orders of magnitude, owing to which their factor of merit is lower than that of stilwellite ceramics. It is only expensive monocrystalline pyroelectrics that have better characteristics. However, the cost of glass ceramic textures is infinitely small compared to the cost of monocrystals. Furthermore, the available base for growing monocrystals with valuable properties, including crystals in the stilwellite system is limited, and some monocrystals cannot be grown to a size sufficient for their technical application. In contrast to the widespread ceramic technology, the glass-ceramic technology makes it possible to obtain materials with crystal anisotropy and a dense microstructure by usual molding methods. To achieve this purpose, oriented crystallization of glass is implemented by thermal treatment of an intermediate piece molded by the hot extrusion method or by heat treatment of a molded product under external field effects of various origins.

The development of spinel and enstatite types of nanoglass ceramics opens prospects for using is as the main component in solid magnetic diskettes for data storage. These types of glass ceramics have a high elasticity modulus (145 GPa), mechanical strength (220 MPa) and low surface roughness (0.5 – 1.0 nm). Glass ceramics have substantial advantages over currently used aluminum coated by NiP and chemically reinforced by aluminosilicate glass: better surface quality is better, higher wear resistance, resistance to vibration at high rotational speeds, and possibility of producing thinner diskettes than the ones based on aluminum and glass.

An example of using glass ceramic material in medicine is provided by bioglass ceramics and materials based on it. A phenomenon recently discovered of the formation of a strong biochemical bond between calcium- and fluorine-containing vitreous and glass-ceramics materials and a live bone tissue, as a consequence of physicochemical and biochemical processes, has opened prospects for the development of artificial biologically active bone implants, endoprosthesis and medical devices of a new generation. The functioning of these materials in a living body resembles the processes of self-organization in a complex nonequilibrium systems. Bioactivity inherent in calcium-phosphate implants and endoprosthesis constitutes a significant advantage over articles made of traditional materials: metals and alloys, plastics, or corundum ceramics. An absence of biochemical binding between traditional materials and adjacent bone tissue leads to the formation of a connective-tissue capsule around and implant and, consequently, gradual weakening of the bond between the implant and the bone, disturbance of continuity between the bone fragment and the implant and, occasionally, inflammatory reactions and detachment of the implant. In contrast, when a bioglass-ceramic implant is used, an interface boundary between the implant and the live bone completely disappears with time and a continuous bone fragment is formed. The tensile strength at the site of joining may reach 40 MPa.

Bioglass ceramics (“biositalls”) are synthesized on the basis of calcium-bearing phosphate or silicophosphate glasses, whose crystallization leads to the formation of main phases represented by calcium phosphates responsible for bioactivity (apatite, oxyfluorapatite, witlokite, etc.) and calcium silicates ensuring mechanical strength (wollastonite, forsterite, diopside) and capacity of material for machine

treatment (fluorophlogopite, muscovite). Bioglass ceramics are close to natural bone in their strength and elastic parameters, the latter being especially significant. This provides for normal functioning of bone tissue under external loading and prevents its reabsorption in the post-surgery period. Low crack resistance typical of glass ceramics is raised to $4 – 5$ MPa $\cdot$ m$^{1/2}$ in biocomposites, in which glass ceramic serves as a matrix reinforced by strengthening fibers, filaments, or disperse particles. To increase mechanical strength of porous materials obtained according to the ceramic technology, one can apply techniques enabling to produce implants with a gradient structure varying from a densely sintered base to porous surface layers.

Different countries currently produce about 10 brands of bioactive glass ceramic materials: Ceravital (USA), Cerabone (Japan), Bioverit, Ilmaplant (Germany), etc. The use of bone implants and endoprostheses made of these materials in prosthetic surgery, stomatology, and orthopedics reduces the rehabilitation period for patients after surgery and decreases the number of repeated surgeries. In future these materials can become a basis for solving one of the most topical problems of the contemporary science of medical materials: the problem of developing artificial bones.

The latest achievement in the development of new glass ceramic materials for medicine are related to the development of magnetic compounds for treatment of bone cancer. A powdered aluminosilicophosphate matrix filled with magnetic microparticles of lithium ferrite or hematite is introduced into bone tissue affected by cancer, after which a magnetic field is activated. As a result, local portions of tissue get heated to a temperature of 43°C and cancerous cells perish (the hypothermia effect).

The promising materials of this class include porous bioglass ceramics impregnated by a medication used to transport the medication to a body organ affected; reabsorbable materials providing for a slow release of copper or silver to prevent bacterial contamination of water; nutritive media with controlled solubility, which can slowly (for several years) release elements needed by plants into soil).

Glass ceramics are of great interest for material-consuming production sectors and the construction industry. Many countries already experience a shortage of natural building materials and facing stones: granite, marble, gabbro, tuff, etc. The problem is being be solved by replacing them by synthesized materials, such as ceramics, stone casting, decorative foam materials. Glass ceramics for construction purposes are gradually taking the niche of synthetic facing and decorative materials: shlakositall, sigran, neoparies, etc. The majority of such materials are produced from naturally abundant silicon, aluminum, calcium, and magnesium oxides, whose prospected resources can satisfy industrial needs for 250 – 300 years to come. In addition to natural raw materials, the synthesis of building glass ceramics extensively involves wastes generated in various sectors of industry: slag from blast furnaces, nonferrous metallurgy, and thermal power plants, wastes from chemical and stone-processing industries. Inclusion of this waste in a mass-scale production of glass ceramics can simultaneously solve a most critical environmental problem of complex processing of materials and disposal of technogenic waste.

Glass ceramics for construction surpass or successfully compete with natural materials in many service properties (mechanical properties, water absorption, chemical and abrasive resistance, cold resistance). For instance, pyroxene glass ceramics typically have high strength parameters together with satisfactory thermal stability and low abradability. Wollastonite slag glass ceramics are resistant to abrasive effect and virtually do not dissolve in acids, whereas melilite and forsterite materials have increased alkali resistance. A coarse-crystalline (2 – 5 mm) spherulite structure of sygran (synthetic granite) and an oriented structure of neoparies impart decorative and architectural expressivity to materials, which in texture resemble natural granite and marble and in their physicochemical properties surpass the latter.

Owing to high resistance to atmospheric effect, solar light, dust, and detergents, glass ceramics intended for construction have an unlimited service life. Water and fire resistance, gas and vapor impermeability, and possibility of easy cleaning make then suitable for wall facing and structural elements, flooring and staircases in civil engineering.

To conclude, it should be noted that expansion of available glass ceramics and their growing role among the contemporary materials are based on research and development carried out in the framework of national programs in various countries. The leading centers in this field are research departments of Corning Glass Works and Owens-Illinois (USA), Schott Glaswerke Mainz (Germany), Nippon Electric Glass Co. Ltd (Japan), Universities of Krakow, Florida, Kioto, Berlin, Naples, Shanghai, and others. Russia for many years has had a leading place in research and industrial production of glass ceramics. However, the general recession of economics and science, the absence of machine-building facilities and virtual suspension glass ceramic production, an abrupt drop in the demand for glass ceramics on part of the defense sector, all had a negative effect on research and implementation of advanced developments in this field. A sustainable progress of glass ceramic materials as part of up-to-date material science in Russia can be achieved only by substantial investments in research and revival of up-to-date industrial production.